


N2C-M1101-EP

noted in the European Search
Report of EP 0371565.7
Your Ref.: N2C-M1101-EP

19  **Europäisches Patentamt**
European Patent Office
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11 Publication number: **0 654 456 A1**

12 **EUROPEAN PATENT APPLICATION**

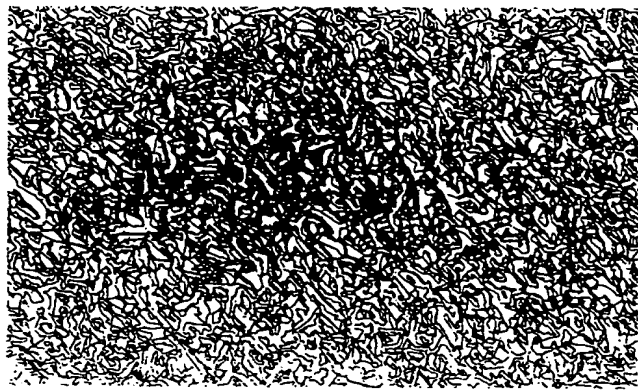
21 Application number: **94117640.6** 51 Int. Cl.⁶: **C04B 35/44, C04B 35/80, C04B 35/117**
22 Date of filing: **09.11.94**

<p>A request for addition of a fourth priority has been filed pursuant to Rule 88 EPC. The request has been allowed.</p> <p>30 Priority: 12.11.93 JP 317242/93 12.11.93 JP 317243/93 15.07.94 JP 193470/94 15.07.94 JP 193471/94</p> <p>43 Date of publication of application: 24.05.95 Bulletin 95/21</p> <p>84 Designated Contracting States: DE FR GB</p> <p>71 Applicant: UBE INDUSTRIES, LTD. 12-32, Nishihonmachi 1-chome Ube-shi, Yamaguchi (JP)</p>	<p>72 Inventor: Waku, Yoshiharu 2-8-1, Higashi-obayama-cho Ube-shi, Yamaguchi (JP) Inventor: Ohtsubo, Hideki 3-10-33, Higashi-kazigaeshi Ube-shi, Yamaguchi (JP) Inventor: Kohtoku, Yasuhiko 4-3-11, Kitasako-shin-machi Ube-shi, Yamaguchi (JP)</p> <p>74 Representative: Hoeger, Stellrecht & Partner Uhlandstrasse 14 c D-70182 Stuttgart (DE)</p>
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54 **Ceramic composite material.**

57 A novel ceramic composite material consisting of single crystal α -Al₂O₃ and polycrystal Y₃Al₅O₁₂ and a ceramic composite material consisting of polycrystal α -Al₂O₃ and polycrystal Y₃Al₅O₁₂, each having a high mechanical strength and creep behavior particularly at high temperature are provided.

Fig.3



50µm

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BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates to a ceramic composite material which has a high mechanical strength and an excellent creep resistance in a wide temperature range from room temperature to high temperature and is suitable to be used as a structural material at a high temperature.

2. Description of the Related Art

10 SiC or Si₃N₄ has been investigated to develop ceramic materials to be used at high temperatures but is not sufficient in high temperature properties. As an alternative material thereof, SiC/SiC composite materials produced by chemical vapor impregnation, provided by Societe Europeene de Propulsion, have attracted attention, at the present are considered to be the best high temperature structural materials and have been
15 investigated and developed. The temperature range at which they can be used is reported to be 1400 °C or lower.

T. Parthasarathy et al. in Journal of the American Ceramics Society Vol. 76, No. 1, pp29 - 32 (1993) disclosed a composite of alumina and yttrium aluminum garnet (sometime hereinafter referred to as "YAG") of eutectic Al₂O₃-Y₃Al₅O₁₂. T. Parthasarathy et al. also disclose a method of producing the composite by
20 unidirectionally melting and solidifying a mixed powder of Al₂O₃ and Y₂O₃ in a crucible.

It is comprehensible from the description on page 29, right column, lines 9 to 10 and Figs. 1 and 2 of the literature that the composite is polycrystalline and includes grain boundaries. This is clearly supported from the description "The failure was usually along the colony boundaries with crack running along the Al₂O₃-YAG interface boundaries". These colony boundaries are shown as portions where the microstructure
25 is larger than in the other portions in Fig. 2 of the literature.

This composite material has stresses equivalent to those of sapphire at 1530 °C and 1650 °C when the strain rate was made constant.

Moreover, the present inventors confirmed in experiments that the composite disclosed by Mr. Parthasarathy et al. includes pores or voids in the microstructure and the mechanical strength of the
30 composite rapidly lowers at high temperature.

Therefore, the object of the present invention is to provide a ceramic composite material comprising polycrystal α -Al₂O₃ and polycrystal Y₃Al₅O₁₂ and a ceramic composite material comprising single crystal α -Al₂O₃ and polycrystal Y₃Al₅O₁₂, which have an excellent mechanical strength and creep behavior from room temperature to high temperature and significantly improved these properties particularly at high
35 temperature.

SUMMARY OF THE INVENTION

The above object is attained in accordance with the present invention by providing a composite material
40 consisting essentially of single crystal α -Al₂O₃ and polycrystal Y₃Al₅O₁₂ (YAG) without a colony and having a three point bending strength at 1500 °C in air of at least 600 MPa and/or a compression creep strength at 1600 °C in air of at least 500 MPa and by providing a composite material consisting essentially of polycrystal α -Al₂O₃ and polycrystal Y₃Al₅O₁₂ without a colony and having a three point bending strength at
45 1500 °C in air of at least 500 MPa.

BRIEF DESCRIPTION OF THE INVENTION

Figs. 1 and 2 are X-ray diffraction patterns of the composite material obtained in Example 1;

Fig. 3 is a photomicrograph of the composite material of Example 1;

50 Fig. 4 is a photomicrograph of the composite material obtained in Comparative Example 1;

Fig. 5 is an X-ray diffraction pattern of the composite material obtained in Example 3;

Fig. 6 is a photomicrograph of the composite material of Comparative Example 3; and

Fig. 7 is a photomicrograph of the composite material of Comparative Example 3.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The term "single crystal" used in the specification means the crystal structure in which only a diffraction peak from a certain crystal plane of α -Al₂O₃ is observed in an X-ray diffraction of the composite

material.

The term "polycrystal α -Al₂O₃" used in the specification means the crystal structure in which diffraction peaks from various crystal planes of α -Al₂O₃ are observed in an X-ray diffraction of the composite material.

The term "without a colony" used in the specification means that there are no coarse polycrystalline grains or no grain boundary phases in the composite material when observed by photomicrography. The colony is a coarse grain or an area defined by a grain boundary phase.

In accordance with the first aspect of the present invention, there is provided a ceramic composite material consisting essentially of single crystal α -Al₂O₃ and polycrystal YAG without a colony and having a three point bending strength at 1500 °C in air of at least 500 MPa.

Fig. 1 is an X-ray diffraction pattern from a plane perpendicular to the solidification direction of the ceramic composite material prepared in Example 1, described later, and Fig. 2 is an X-ray diffraction pattern from a plane declined by about 81° from the solidification direction of the same ceramic composite material (no diffraction peak of Al₂O₃ was obtainable from an angle perpendicular to the solidification direction).

Fig. 1 shows diffraction peaks at $2\theta = 18.06^\circ$, 20.88° , 36.58° , 38.16° , 49.1° , 56.22° and 60.64° corresponding respectively to (211), (220), (422), (431), (541), (721) and (651) planes of YAG.

Fig. 2 shows for Al₂O₃ only a diffraction peak at $2\theta = 37.8^\circ$ corresponding to (110) plane and, for YAG, diffraction peaks at $2\theta = 20.74^\circ$, 42.5° , 54.92° and 65.88° corresponding to (220), (440), (640) and (660) planes respectively.

The facts clearly indicate that the ceramic composite material of the first aspect of the present invention consists of single crystal α -Al₂O₃ and polycrystal YAG.

Fig. 3 is a photomicrograph of the ceramic composite material obtained in Example 1, described later, in which no colony, grain boundary phase or coarse grain is observed, in contrast to Figs. 1 and 2 of Parthasarathy et al.'s literature.

On the other hand, Fig. 4 is a photomicrograph of the ceramic composite material obtained in Comparative Example 1, in which colonies, grain boundary phases or coarse grains as shown in Figs. 1 and 2 of Parthasarathy's literature are observed.

In the ceramic composite material of the first aspect of the present invention, the single crystal α -Al₂O₃ and polycrystal YAG form a uniform sea/island structure when a cross-sectional microstructure is observed. It is not certain but is considered that the sea is single crystal α -Al₂O₃ and the island is polycrystal YAG. The sizes of the sea and islands may be varied and controlled by selecting the solidification conditions, but are typically in a range of 5 to 50 μ m.

The amounts of single crystal α -Al₂O₃ and polycrystal YAG in the composite material of the first aspect of the present invention can be varied in ranges of about 20 to 80% by volume of single crystal α -Al₂O₃ and about 80 to 20% by volume of polycrystal YAG, by changing the proportion between the Al₂O₃ and YAG starting powders. The eutectic composition is 55% by volume of Al₂O₃ and 45% by volume of YAG.

The ceramic composite material of the first aspect of the present invention has a three point bending strength at 1500 °C in air of at least 600 MPa and preferably has a compression creep strength at 1600 °C in air of at least 500 MPa.

In accordance with the second aspect of the present invention, there is provided a ceramic composite material consisting essentially of polycrystal α -Al₂O₃ and polycrystal YAG without a colony and having a three point bending strength at 1500 °C in air and a compression creep strength at 1600 °C in air of at least 500 MPa.

Fig. 5 is an X-ray diffraction pattern from a plane perpendicular to the solidification direction of the ceramic composite material prepared in Example 3, described later.

Fig. 5 shows diffraction peaks at $2\theta = 18.1^\circ$, 27.8° , 29.78° , 33.26° , 36.63° , 38.22° , 41.18° , 46.62° , 51.6° , 55.28° , 56.26° , 60.7° and 69.06° corresponding to (211), (321), (400), (420), (422), (431), (521), (532), (631), (640), (721), (651) and (752) respectively, for YAG.

Fig. 4 also shows diffraction peaks at $2\theta = 26.62^\circ$, 37.78° , 52.7° and 59.78° corresponding to (012), (110), (024) and (211) planes of Al₂O₃.

These facts clearly indicate that the ceramic composite material of the present invention consists of polycrystal α -Al₂O₃ and polycrystal YAG.

Fig. 6 is a photomicrograph of the ceramic composite material obtained in Example 3, in which no colony, grain boundary phase or coarse grain is observed.

In the ceramic composite material of the second aspect of the present invention, the polycrystal α -Al₂O₃ and polycrystal YAG form a uniform sea/island structure when a cross-sectional microstructure is observed. It is not certain but is considered that the sea is polycrystal α -Al₂O₃ and the island is polycrystal YAG. The sizes of the sea and islands may be varied and controlled by selecting the solidification

conditions, but are typically in a range of 1 to 50 μm .

The amounts of polycrystal $\alpha\text{-Al}_2\text{O}_3$ and polycrystal YAG in the composite material of the second aspect of the present invention can be varied in ranges of about 20 to 80% by volume of single crystal $\alpha\text{-Al}_2\text{O}_3$ and about 80 to 20% by volume of single crystal YAG, by changing the proportion between the Al_2O_3 and YAG starting powders. The eutectic composition is 55% by volume of Al_2O_3 and 45% by volume of YAG.

The ceramic composite material of the second aspect of the present invention has a three point bending strength at 1500 °C in air of at least 500 Ma and/or a compression creep strength at 1600 °C in air of at least 500 MPa.

The ceramic composite material of the present invention can be produced; for example, by the following process.

A mixed powder of $\alpha\text{-Al}_2\text{O}_3$ and Y_2O_3 powders in a ratio for a desired ceramic composite material is prepared by weighing and mixing. The mixing method is not particularly limited and may be either of a dry mixing method or a wet mixing method. In a wet mixing method, alcohol such as methanol and ethanol is generally used as a medium.

The mixed powder is then heated to a temperature at which both starting powders are molten, for example, at 1800 to 2500 °C, in a conventional furnace, for example, an arc furnace to melt the mixed powder.

Subsequently, the melt is charged in a crucible and then unidirectionally solidified to prepare a ceramic composite material of the present invention. Alternatively, the melt is once solidified and crushed and the crushed material is then charged in a crucible and melted and unidirectionally solidified.

The atmospheric pressure during the melting and solidification is generally 10^{-3} Torr or less, preferably 10^{-4} Torr or less. The speed of moving the crucible for unidirectional solidification, i.e., the rate of growth of the ceramic composite material is generally more than 50 mm/hour to 200 mm/hour for the ceramic composite material consisting essentially of single crystal $\alpha\text{-Al}_2\text{O}_3$ and polycrystal YAG of the first aspect of the present invention, and generally more than 200 mm/hour to 1000 mm/hour for the ceramic composite material consisting essentially of polycrystal $\alpha\text{-Al}_2\text{O}_3$ and polycrystal YAG of the second aspect of the present invention. The control of the conditions other than the atmospheric pressure and crucible moving speed can be done in the same manner as in conventional methods.

If the atmospheric pressure or the crucible moving speed during the melting and solidification is outside the above ranges, pores or voids tend to appear at colony boundaries, and it is difficult to obtain a composite material excellent in mechanical strength and creep behavior.

The apparatus for unidirectional solidification may be a conventional one in which a crucible is vertically movably mounted in a vertically arranged cylindrical container, an induction heating coil is disposed around the approximate center position of the cylindrical container, and a vacuum pump is provided to evacuate the container space.

EXAMPLES

Example 1

$\alpha\text{-Al}_2\text{O}_3$ powder (Sumitomo Chemical Co., Ltd., AKP-30) and Y_2O_3 powder (Shin-etsu Chemical Co. Ltd., sub-micron type) in a molar ratio of 82% of the former to 18% of the latter were milled in a wet ball mill using ethanol. The obtained slurry was dried in a rotary evaporator to remove ethanol.

The obtained mixed powder of $\alpha\text{-Al}_2\text{O}_3$ and Y_2O_3 was charged in a crucible placed in a chamber, in which the atmospheric pressure was maintained at 10^{-5} Torr and the crucible was heated by an induction coil to 1850 to 1900 °C to melt the mixed powder in the crucible. Subsequently, unidirectional solidification was conducted by descending the crucible at a speed of 60 mm/hour under the above atmospheric pressure to obtain a ceramic composite material.

Figs. 1 and 2 show X-ray diffraction patterns of the composite material obtained from planes perpendicular to and declined by about 81° from the solidification direction of the composite material. Diffraction peaks from polycrystal YAG are observed in Fig. 1 and only a diffraction peak from (110) plane of single crystal $\alpha\text{-Al}_2\text{O}_3$ is observed in Fig. 2, which demonstrates that the above composite material consists of single crystal $\alpha\text{-Al}_2\text{O}_3$ and polycrystal YAG.

Fig. 3 is a photomicrograph of the composite material. Fig. 3 demonstrates that the composite material does not include any colony or grain boundary phase, pores or voids do not exist, and a uniform sea/island structure is formed.

The mechanical strengths of the composite material are shown in Table 1, where the three point bending strength and compressive creep strength were measured in air.

This composite material had a weight gain of 0.007 mg/cm³ after kept at 1700 °C in air for 100 hours.

5 Example 2

The procedures in Example 1 were repeated except the atmospheric pressure in the chamber and the descending speed of the crucible were changed to 1×10^{-3} Torr and 100 mm/hour.

10 The X-ray diffraction patterns from the plane perpendicular to and declined by 9° from the direction of solidification of the composite material were the same as in Fig. 1, and in Fig. 2 respectively, indicating that the composite material consisted of single crystal α -Al₂O₃ and polycrystal YAG.

A photomicrograph of this composite material showed that the composite material contains no colony or grain boundary phase, and no pores or voids, and forms a uniform sea/island structure.

15 The mechanical strengths of this composite material are shown in Table 1. The composite material had a weight gain of 0.007 mg/cm³ after kept at 1700 °C in air for 100 hours.

Comparative Example 1

20 The procedures of Example 1 were repeated except that the pressure in the chamber was normal or atmospheric pressure.

Fig. 4 shows a photomicrograph of the obtained ceramic composite material.

Fig. 4 shows that the composite material has colonies or grain boundary phases and voids.

The mechanical strengths of the composite material are shown in Table 1.

The composite material had a weight gain of 0.02 mg/cm³ after kept at 1700 °C in air for 100 hours.

25 Table 1

	Example 1	Example 2	Comparative Example 1
30 Three point bending strength (MPa)			
at 1500 °C	670	640	320
at 1600 °C	655	635	250
at 1700 °C	610	590	210
35 Compressive creep strength at 1600 °C (MPa):			
at Strain rate 1×10^{-4} sec ⁻¹	610	600	270
at Strain rate 1×10^{-5} sec ⁻¹	570	550	210

40 Example 3

The procedures of Example 1 were repeated except that the descending speed of the crucible was 220 mm/hour to obtain a ceramic composite material.

45 Fig. 5 is an X-ray diffraction pattern from the plane of the composite material perpendicular to the direction of solidification thereof. Fig. 5 shows diffraction peaks from polycrystal α -Al₂O₃ and polycrystal YAG, indicating that α -Al₂O₃ and YAG were polycrystals.

Fig. 6 is a photomicrograph of the composite material, in which no colony or grain boundary phase was observed and a uniform sea/island structure was formed.

50 The mechanical strengths of the composite material are shown in Table 2. In Table 2, the three point bending strength and the compression creep strength were measured in air.

The composite material had a weight gain of 0.004 mg/cm³ after kept at 1700 °C in air for 100 hours.

Example 4

55 The procedures in Example 1 were repeated except that the atmospheric pressure in the chamber and the descending speed of the crucible were changed to 10^{-3} Torr and 300 mm/hour to obtain a ceramic composite material.

The X-ray diffraction pattern of the composite material from the plane perpendicular to the direction of solidification was the same as Fig. 5, indicating that the composite material consisted of polycrystal α -Al₂O₃ and polycrystal YAG.

In a photomicrograph of the composite material, no colony or grain boundary phase and no pore or void was observed, and a uniform sea/island structure was formed.

The mechanical strengths of the composite material are shown in Table 2.

The composite material had a weight gain of 0.005 mg/cm³ after kept at 1700 °C in air for 100 hours.

Comparative Example 2

The procedures of Example 3 were repeated except that the pressure in the chamber was normal or atmospheric pressure.

Fig. 7 is a photomicrograph of the obtained ceramic composite material.

Fig. 7 shows that the composite material has colonies or grain boundary phases and voids.

The mechanical strengths of the composite material are shown in Table 2.

The composite material had a weight gain of 0.005 mg/cm³ after kept at 1700 °C in air for 100 hours.

Table 2

	Example 3	Example 4	Comparative Example 2
Three point bending strength (MPa)			
at 1500 °C	550	530	320
at 1600 °C	510	490	250
at 1700 °C	480	450	210
Compressive creep strength at 1600 °C (MPa):			
at Strain rate $1 \times 10^{-4} \text{ sec}^{-1}$	600	590	270
at Strain rate $1 \times 10^{-5} \text{ sec}^{-1}$	540	520	210

Claims

1. A ceramic composite material consisting essentially of single crystal α -Al₂O₃ and polycrystal Y₃Al₅O₁₂ without a colony and having a three point bending strength at 1500 °C in air of at least 600 MPa and/or a compression creep strength at 1600 °C in air of at least 500 MPa.
2. A ceramic composite material according to claim 1 wherein said single crystal α -Al₂O₃ and said polycrystal Y₃Al₅O₁₂ form a uniform sea/island structure in which sea and islands have a size of 5 to 50 μm .
3. A ceramic composite material according to claim 1 wherein said composite material comprises 20 to 80% by volume of the single crystal α -Al₂O₃ and 80 to 20% by volume of the polycrystal Y₃Al₅O₁₂.
4. A ceramic composite material according to claim 1 wherein said composite material does not include pores or voids.
5. A ceramic composite material consisting essentially of polycrystal α -Al₂O₃ and polycrystal Y₃Al₅O₁₂ without a colony and having a three point bending strength at 1500 °C in air of at least 500 MPa.
6. A ceramic composite material according to claim 5 wherein said composite material comprises 20 to 80% by volume of the polycrystal α -Al₂O₃ and 80 to 20% by volume of the polycrystal Y₃Al₅O₁₂.
7. A ceramic composite material according to claim 5 wherein said polycrystal α -Al₂O₃ and the polycrystal Y₃Al₅O₁₂ form a uniform sea/island structure in which sea and islands have a size of 1 to 50 μm .

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8. A ceramic composite material according to claim 5 wherein said composite material does not include pores and voids.
9. A ceramic composite material according to claim 5 wherein said composite material has a compression creep strength at 1600 °C in air of at least 500 MPa.

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Fig.1

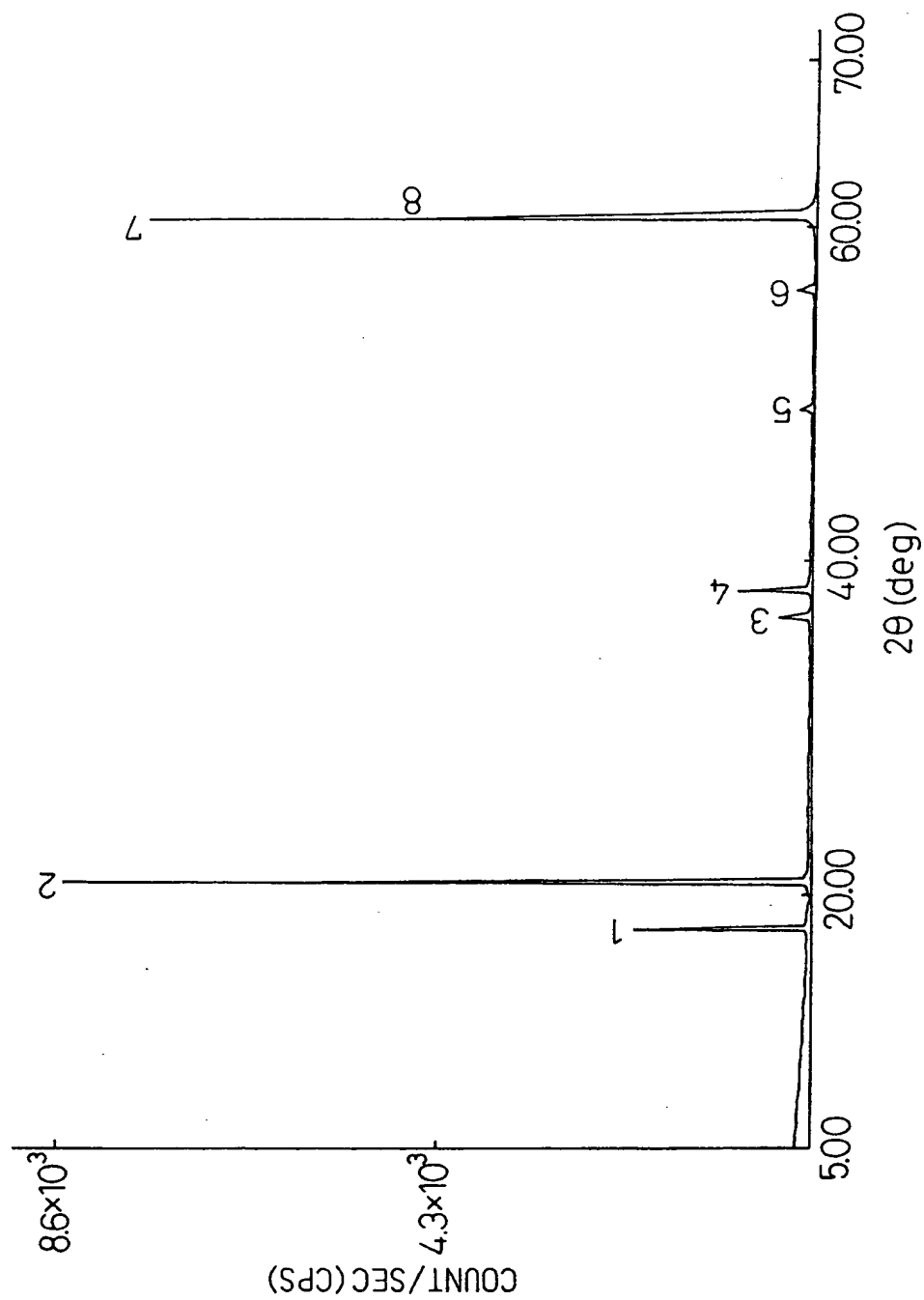


Fig. 2

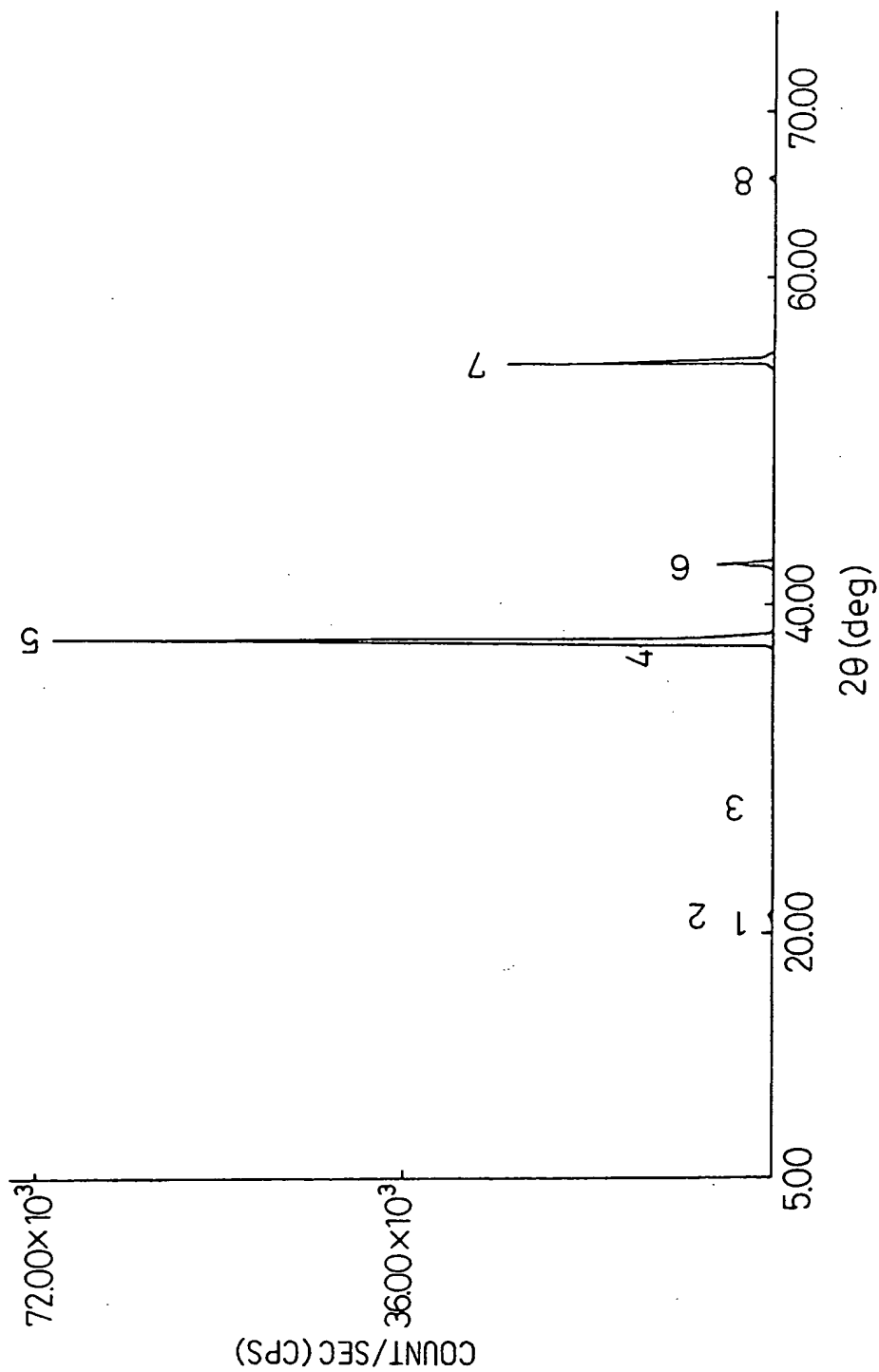
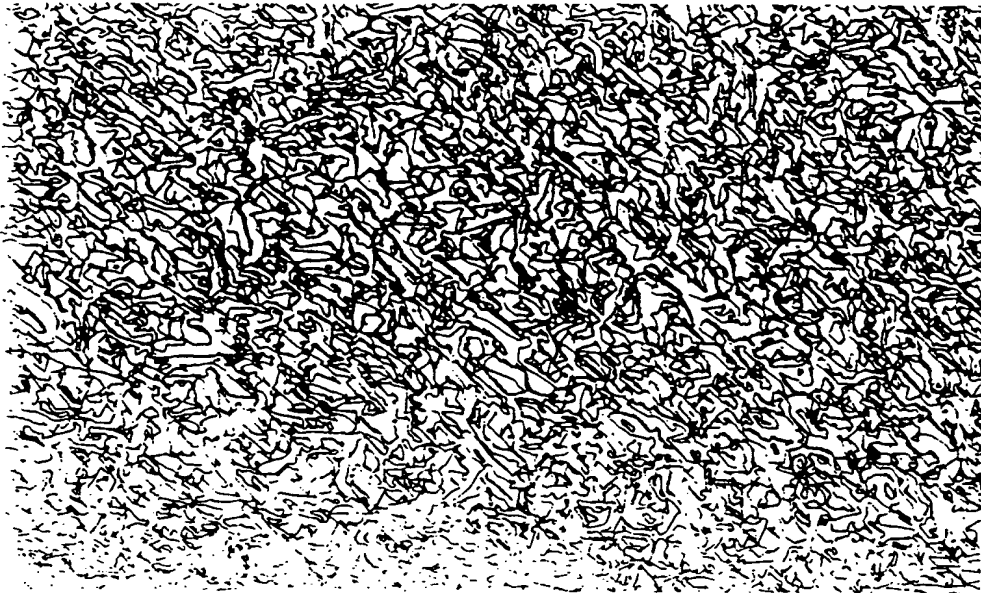


Fig.3



50µm

Fig.4



Fig. 5

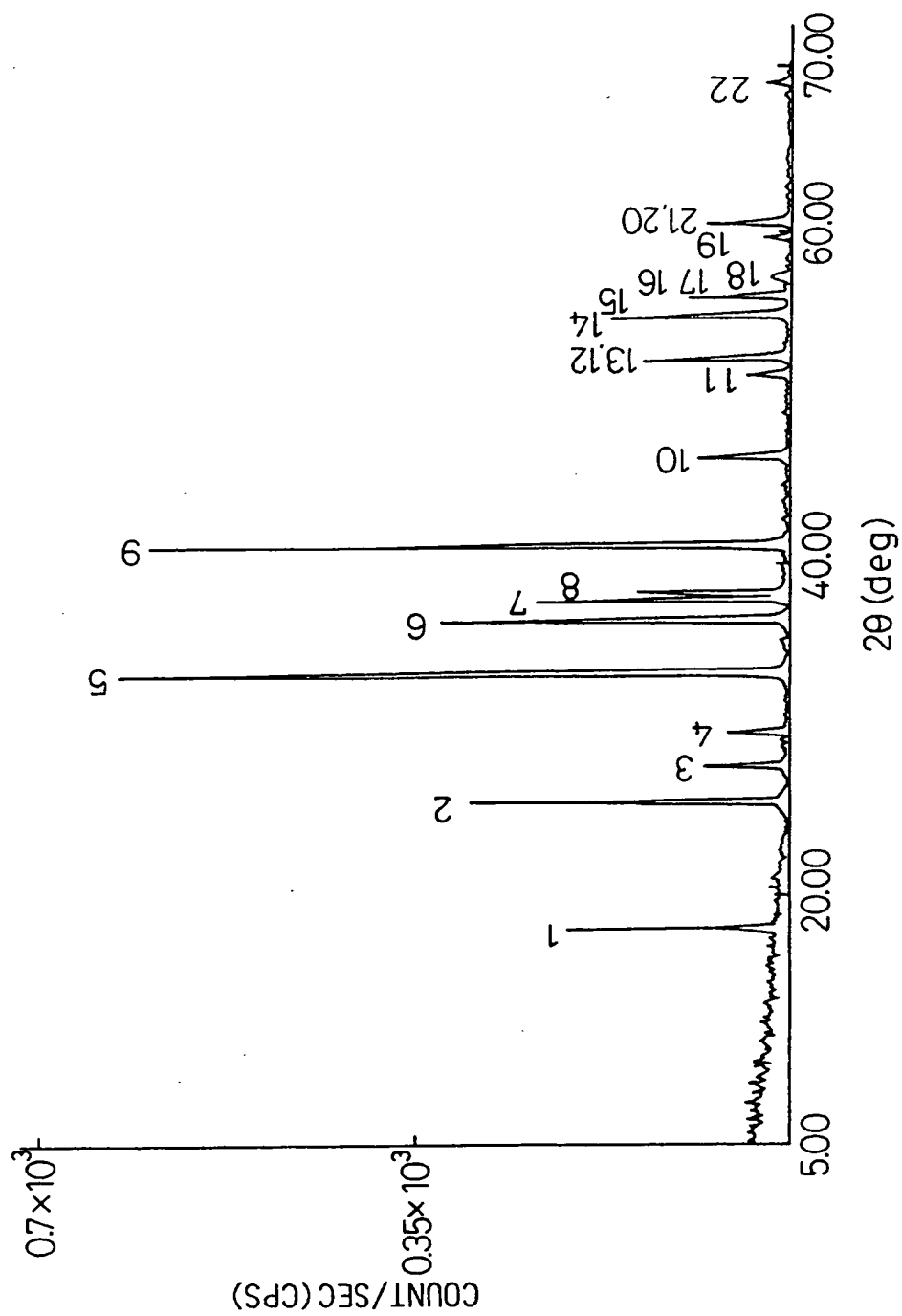
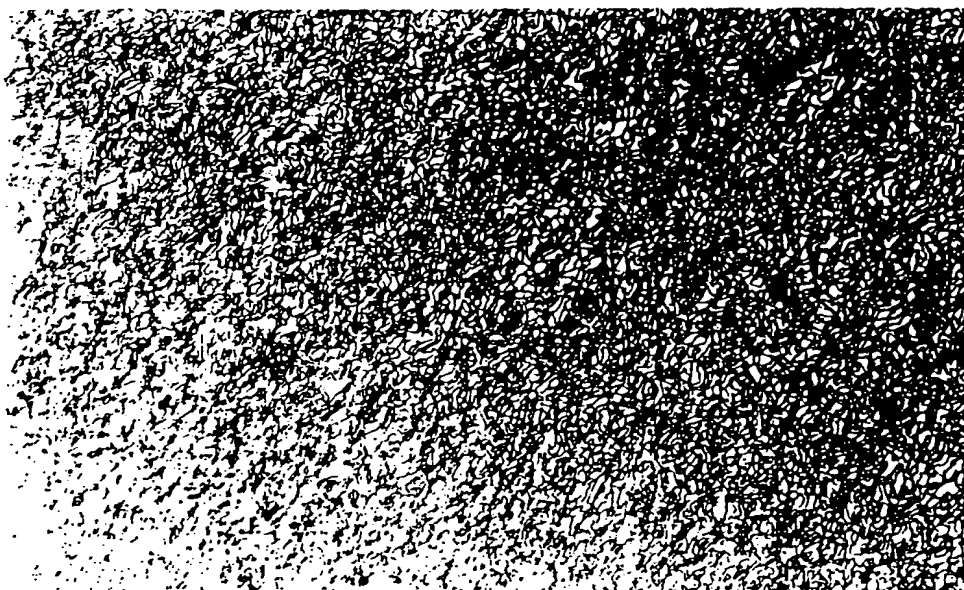
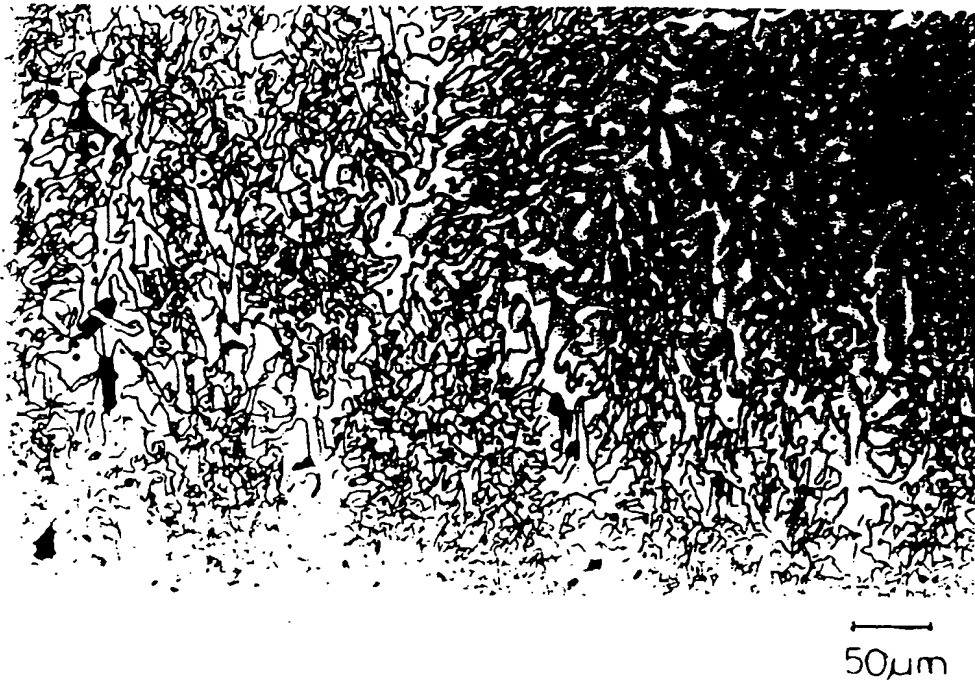


Fig. 6



—
50μm

Fig.7





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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X,D	JOURNAL OF THE AMERICAN CERAMIC SOCIETY, vol.76, no.1, 1993 pages 29 - 32 T.A.PARTHASARATHY ET AL. * the whole document *	1-9	C04B35/44 C04B35/80 C04B35/117
A	US-A-3 653 432 (F.SCHMID ET AL.) * claims 1-6,14 *	1-9	
A	CHEMICAL ABSTRACTS, vol. 116, no. 6, 10 February 1992, Columbus, Ohio, US; abstract no. 49098r, KAWAKAMI 'DIRECTIONAL SOLIDIFICATION OF THE ALUMINA-YTTRIUM ALUMINIUM GARNET EUTECTIC BY THE FLOATING ZONE METHOD' page 541 ;column R ; * abstract * & NAGOYA KOGYO GIJUTSU SHIKENSHO HOKOKU, vol.40, no.1, 1991, JAPAN pages 54 - 58		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C04B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 February 1995	Examiner Harbron, J
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